

Process for the preparation of polyorganosilylated
carboxylate monomers or polymers thereof

Field of the invention

The invention relates to an improved method for the
5 preparation of polyorganosilylated carboxylate monomers or
polymers. The invention further relates to said obtained
polyorganosilylated carboxylate monomers or polymers and
in another aspect, the invention relates to their use for
the synthesis of hydrolysable polymers, such as binders
10 for modern antifouling coatings.

Background to the invention

Antifouling paints are used in general to prevent and
delay the fouling of underwater structures (e.g. ships'
bottom, docks, fishnets, and buoys) caused by various
15 marine organisms such as shells, seaweed and aquatic
bacteria. When such aquatic organisms adhere and propagate
on an underwater structure like the bottom of a ship, the
surface roughness of the whole ship may be increased to
induce decrease of velocity of the ship and subsequently
20 increase of fuel consumption. The removal of these aquatic
organisms from the ship's bottom requires much labour and
a long period of working time. In addition, if these
aquatic organisms adhere and propagate on an underwater
structure such as a steel structure they deteriorate their
25 anticorrosive coating films leading to a reduction of the
lifetime of the underwater structure.

Underwater structures are therefore preferably coated with
an antifouling paint employing polymers containing various
hydrolysable groups and more specifically organosilyl
30 groups. Several antifouling paints are known.

EP 0 297 505 for example relates to an antifouling paint that contains a polymer having organosilyl groups and/or organopolysiloxane groups in side chains. Since the organopolysiloxane group is derived from dehydrating
5 condensation or like means of silicon oil with methacrylic acid, this document refers to a mixture of oligomers having different numbers of the recurrence of the organosiloxane group.

WO 84/02915 and JP 63215780 describe an antifouling paint
10 of the hydrolysable self-polishing type employing a methacrylic ester polymer having triorganosilyl group in side chains or a similar polymer. Other examples related to the use of organosilyl acrylate polymers in antifouling compositions are EP 1 127 902, EP 1 127 925, JP 63118381,
15 WO 96/38508, EP 0 802 243, EP 0 714 957, JP 07018216, JP 01132668, JP 01146969 and US Pat. No. 4,957,989 hereby incorporated by reference.

The polymers used in the above-described antifouling paints are based on silylated carboxylate monomers.

20 Several processes are known as conventional techniques for the synthesis of said silylated carboxylate monomers.

JP 5306290 for example describes a process to obtain a methacrylic functional group-containing organosilicon compound. The process comprises reacting methacrylic acid
25 with a halogenoalkylsilane e.g. trialkylsilylchloride in the presence of a tertiary amine compound having a cyclic structure. This process has disadvantages such as the reduced availability and storage stability of the silyl chloride. Moreover, the reaction yields as a by-product a
30 hydrogen halide, which provokes the corrosion of the production equipment, or a halide salt, which has to be removed by filtration.

The synthesis of trimethylsilyl methacrylate from methacrylic acid and trimethylsilyl chloride is disclosed in Fedotov. et. al. Zh.Prikl.Khim.(1971), 44(3),695. The synthesis of trimethylsilyl methacrylate from methacrylic acid and hexamethyldisilazane is described in A. Chapman & A.D. Jenkins J.Polym.Sci. Polym.Chem.Edn. vol 15, p.3075 (1977). This method has the disadvantage of producing ammonia.

JP 10195084 discloses the reaction of unsaturated carboxylic acid such as acrylic acid or methacrylic acid with a trialkylsilylhydride compound in the presence of a copper catalyst. One of the disadvantages of this method is the risk of hydrogenation of the unsaturated carboxylic acid due to a side reaction of the produced H₂ on the carbon-carbon double bond.

US Pat. No. 6,063,887 describes 1-acyloxy-organotetrasiloxane obtained by the reaction of hexamethylcyclotrisiloxane with an acyloxysilane.

An object of the present invention is to provide a novel process capable of readily preparing polyorganosilylated carboxylate monomers or polymers thereof in a high yield from easily available starting materials.

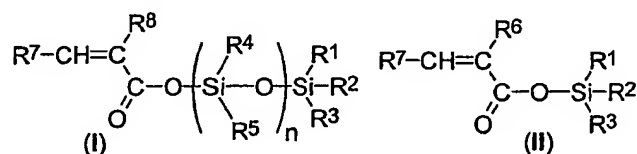
Another object of the present invention is to provide a more direct method for the synthesis of such polyorganosilylated carboxylate monomers or polymers thereof, with easy work-up procedures.

A further object of the present invention is to provide a novel process offering an improvement vis-à-vis of the disadvantages disclosed above.

Summary of the invention

The present invention relates to a process for the preparation of polyorganosilylated carboxylate monomers of general formula (I) or polymers thereof, comprising the

steps of reacting a cyclosiloxane of formula $(R^4R^5SiO)_n$ with an unsaturated organosilylated carboxylate of formula (II) or a copolymer or a polymer thereof under the presence of a suitable catalyst, wherein R^1 , R^2 , R^3 , R^4 , R^5 each independently represent hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, aryl, aralkyl or halogen radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, aralkyl, aryl, hydroxy, halogen, amino or amino alkyl radicals, R^6 represents hydrogen, alkyl radical or $-CH_2-CO_2-SiR^1R^2R^3$, R^7 represents hydrogen, alkyl radical or $-COOR^9$ wherein R^9 represents an alkyl group, R^8 represents hydrogen, alkyl radical or $-CH_2-CO_2-(SiR^4R^5O)_n-SiR^1R^2R^3$, and n represents a number of dihydrocarbylsiloxane units from 3 to 20.



According to an embodiment of the present invention, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^9 are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl. Preferably R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^9 are methyl.

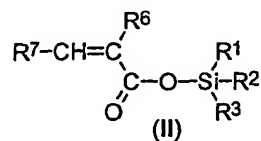
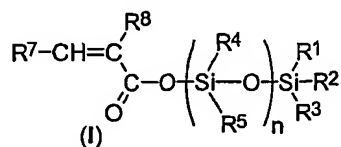
According to another embodiment of the present invention, n represents a number of dihydrocarbylsiloxane units from 3 to 12, preferably from 3 to 8, more preferably from 3 to 6. In a preferred embodiment n is 3.

It was surprisingly found that by reacting cyclosiloxane with unsaturated organosilylated carboxylate monomers, polymers or copolymers thereof, polyorganosilylated carboxylates could be synthesized, when unsaturated

organosilylated carboxylates are known to be not very reactive compounds and to polymerise easily.

Detailed Description of the Invention

The present invention relates to a new process for the synthesis of polyorganosilylated carboxylate monomers of general formula (I) or polymers thereof, wherein a cyclosiloxane of formula $(R^4R^5SiO)_n$ is reacted with an unsaturated organosilylated carboxylate of formula (II) or copolymers or polymers thereof under the presence of a suitable catalyst, wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 have the same meaning as that defined above.



The process of the invention has the advantage of producing polyorganosilylated carboxylate monomers or polymers with exactly the desired number of the dihydrocarbylsilyloxane units.

The process according to the invention is characterized by a specific telomerisation. It was surprisingly found that the telomerisation of cyclosiloxane could be performed with unsaturated organosilylated carboxylate, which are not very reactive compounds and are known to polymerise easily.

The term 'telomerisation' as used herein refers to a process yielding low molecular weight monomers consisting of a chain of a limited number of units terminated at each end by a radical of a different compound (the telogen). See Oxford English Dictionary, Second Ed., Clarendon, Oxford, 1989. The telomerisation reaction proceeds as a polymerisation reaction between two

substances providing respectively the terminal groups and internal linkages of the resulting telomer molecule.

As used herein, the term "polymer" refers to the product of a polymerisation reaction, and is inclusive of
5 homopolymers, copolymers, terpolymers, etc.

As used herein, the term "copolymer" refers to polymers formed by the polymerisation reaction of at least two different monomers.

As used herein, the term "independently selected"
10 indicates that the each radical R so described, can be identical or different. For example each R⁴ in compound of formula (I) may be different for each value of n.

The term "alkyl", as used herein, relates to saturated hydrocarbon radicals having straight, branched or cyclic
15 moieties or combinations thereof and contains 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, still more preferably 1 to 6 carbon atoms, yet more preferably 1 to 4 carbon atoms. Examples of such radicals include methyl, ethyl, n-propyl,
20 isopropyl n-butyl, isobutyl, set-butyl, tert-butyl, 2-methylbutyl, pentyl, iso-amyl, hexyl, cyclohexyl, 3-methylpentyl, octyl and the like.

The term "alkenyl", as used herein, relates to hydrocarbon radicals having one or several double bonds, having
25 straight, branched or cyclic moieties or combinations thereof and containing from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of
30 alkenyl groups include vinyl, allyl, isopropenyl, pentenyl, hexenyl, heptenyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, 1-propenyl, 2-butenyl, 2-

methyl-2-butenyl, isoprenyl, farnesyl, geranyl, geranylgeranyl and the like.

The term "alkynyl", as used herein, relates to hydrocarbon radicals having one or several triple bonds, having
5 straight, branched or cyclic moieties or combinations thereof and having from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably from 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of alkynyl
10 radicals include ethynyl, propynyl, (propargyl), butynyl, pentynyl, hexynyl and the like.

The term "aryl" as used herein, relates to an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, and includes any monocyclic or bicyclic
15 carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. Said radical may be optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aryl includes phenyl, p-tolyl, 4-
20 methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-
25 methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and
30 the like.

The term "aralkyl" as used herein, relates to a group of the formula alkyl-aryl, in which alkyl and aryl have the same meaning as defined above. Examples of aralkyl

radicals include benzyl, phenethyl, dibenzylmethyl, methylphenylmethyl, 3- (2-naphthyl)-butyl, and the like.

The process according to the invention consists of subjecting a cyclosiloxane of formula $(R^4R^5SiO)_n$ to a
5 ring-opening reaction with an unsaturated organosilylated carboxylate of formula (II) or a copolymer or a polymer thereof, in the presence of a suitable catalyst and with or without solvent. The reaction is preferably set up in such a way that each mole of cyclosiloxane is treated with
10 at least one mole of unsaturated organosilylated carboxylate of formula (II) or with a copolymer or a polymer of said carboxylate.

The reaction can be performed with or without solvents. Suitable solvents which can be used in the process
15 according to the invention are nonpolar inert solvents such as for example benzene, toluene, xylene, mesitylene or ethylbenzene, aliphatic hydrocarbons, typically pentane, hexane, cyclohexane, heptane, octane, decane or decahydronaphthalene, noncyclic ethers, typically diethyl
20 ether, diisopropyl ether, diisopropyl ether or diisobutyl ether, or mixtures thereof. In a preferred embodiment, said solvent is toluene.

Examples of the cyclosiloxanes which may be employed in the present process are described in the "Encyclopedia of
25 Polymer Science and Engineering", Mark et al., eds., 2nd ed., John Wiley & Sons (1989), Vol. 15, p.207 et seq., the contents of which are incorporated by reference herein.

Examples of suitable cyclosiloxanes of formula $(R^4R^5SiO)_n$ for use in the process according to the invention include
30 but is not limited to 1,1,3,3,5,5-hexamethyl-cyclotrisiloxane (D3), 1,1,3,3,5,5-hexaethyl-cyclotrisiloxane, 1,1,3,3,5,5-hexaphenyl-cyclotrisiloxane, 1,1,3,3,5,5-hexavinyl-cyclotrisiloxane, 1,3,5-trimethyl-

1,3,5-trivinyl-cyclotrisiloxane, 1,3,5-trimethyl-1,3,5-
 triphenyl-cyclotrisiloxane, 1,3,5-trimethyl-1,3,5-
 tripropyl-cyclotrisiloxane, 1,3,5-triethyl-1,3,5-
 trimethyl-cyclotrisiloxane, 1,3,5-trimethyl-1,3,5-
 5 triphenethyl-cyclosiloxane, 1,3,5-trivinyltrihydro-
 cyclotrisiloxane, 1,3,5-trimethyltrihydro-
 cyclotrisiloxane, pentamethyl-cyclotrisiloxanes, 1,3,5-
 trimethyl-1,3,5-tris(3',3',3'-trifluoropropyl)-
 cyclotrisiloxane (F3), 1,1,3,3,5,5,7,7-octamethyl-
 10 cyclotetrasiloxane (D4), 1,1,3,3,5,5,7,7-octaphenyl-
 cyclotetrasiloxane, 1,1,3,3,5,5,7,7-octavinyl-
 cyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-
 tetrahydro-cyclotetrasiloxane, 1,3,5,7-tetramethyl-
 1,3,5,7-tetra(1-octyl)-cyclotetrasiloxane, 1,3,5,7-
 15 tetravinyl-1,3,5,7-tetramethyl-cyclotetrasiloxane,
 1,3,5,7-tetravinyl-1,3,5,7-tetraethyl-cyclotetrasiloxane,
 1,3,5,7-tetraethyl-1,3,5,7-tetraphenyl-cyclotetrasiloxane,
 1,3,5,7-tetra(1-hexadecyl)-1,3,5,7-tetramethyl-
 cyclotetrasiloxane, 1,3,5,7-tetraoctyltetrahydro-
 20 cyclotetrasiloxane, 1,3,5,7-tetravinyltetrahydro-
 cyclotetrasiloxane, 1,3,5,7-tetraethyltetrahydro-
 cyclotetrasiloxane, 1,3,5,7-tetrapropenyltetrahydro-
 cyclotetrasiloxane, 1,3,5,7-tetrapentenyltetrapentyl-
 cyclotetrasiloxane, 1,3,5,7-tetraphenyltetrahydro-
 25 cyclotetrasiloxane, pentamethyl-cyclotetrasiloxanes,
 hexamethyl-cyclotetrasiloxanes, 1,3,5,7-tetramethyl-
 1,3,5,7-tetrakis(3',3',3'-trifluoropropyl)-
 cyclotetrasiloxane (F4) 1,1,3,3,5,5,7,7,9,9-decamethyl-
 cyclopentasiloxane (D5), 1,3,5,7,9-pentavinyl-1,3,5,7,9-
 30 pentamethyl-cyclopentasiloxane, 1,3,5,7,9-pentadecenyl-
 1,3,5,7,9-pentapropyl-cyclopentasiloxane, 1,3,5,7,9-
 pentamethylpentahydro-cyclopentasiloxane, 1,3,5,7,9-
 pentavinylpentahydro-cyclopentasiloxane, tetramethyl-

cyclopentasiloxanes, hexamethyl-cyclopentasiloxanes,
 heptamethyl-cyclopentasiloxanes,
 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-cyclohexasiloxane
 (D6), 1,3,5,7,9,11-hexavinylhexamethyl-cyclohexasiloxane,
 5 1,3,5,7,9,11-hexamethylhexahydro-cyclohexasiloxane,
 tetramethyl-cyclohexasiloxanes, pentamethyl-
 cyclohexasiloxanes, 1,3,5,7,9,11,13,15,17,19-
 decavinyldecahydro-cyclodecasiloxane,
 1,3,5,7,9,11,13,15,17,19,21,23,25,27,29-
 10 pentadecavinylpentadecahydro-cyclopentadecasiloxane and
 the like.

In a preferred embodiment, said cyclosiloxane of formula
 $(R^4R^5SiO)_n$ is selected from the group comprising
 1,1,3,3,5,5-hexamethyl-cyclotrisiloxane (D3),
 15 1,1,3,3,5,5,7,7-octamethyl-cyclotetrasiloxane (D4),
 1,1,3,3,5,5,7,7,9,9-decamethyl-cyclopentasiloxane (D5),
 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-cyclohexasiloxane
 (D6). More preferably said cyclosiloxane of formula
 $(R^4R^5SiO)_n$ is 1,1,3,3,5,5-hexamethyl-cyclotrisiloxane (D3).

20 Examples of the unsaturated organosilylated carboxylate of
 formula (II) which can be used in the process according to
 the invention include but are not limited to
 trimethylsilyl (meth)acrylate, tri-t-butylsilyl
 (meth)acrylate, tribenzylsilyl (meth)acrylate,
 25 triethylsilyl (meth)acrylate, tri-isopropylsilyl
 (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-n-
 amylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate,
 tri-n-dodecylsilyl (meth)acrylate, tri-n-hexylsilyl
 (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-
 30 propylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate,
 tri-p-methylphenylsilyl (meth)acrylate,
 dibutylcyclohexylsilyl (meth)acrylate, dibutylphenylsilyl
 (meth)acrylate; dicyclohexylphenylsilyl (meth)acrylate,

diisopropyl-n-butylsilyl (meth)acrylate,
 diisopropylstearylsilyl (meth)acrylate, dimethylbutylsilyl
 (meth)acrylate, dimethylcyclohexylsilyl (meth)acrylate,
 dimethylhexylsilyl (meth)acrylate, dimethyloctylsilyl
 5 (meth)acrylate, dimethylphenylsilyl (meth)acrylate,
 ethyldibutylsilyl (meth)acrylate, ethyldimethylsilyl
 (meth)acrylate, lauryldiphenylsilyl (meth)acrylate,
 methyldibutylsilyl (meth)acrylate, n-octyldi-n-butylsilyl
 (meth)acrylate, t-butyl dimethylsilyl (meth)acrylate t-
 10 butyldiphenylsilyl (meth)acrylate, bis(trimethylsilyl)
 itaconate, t-butyldiphenylsilyl methyl fumarate, t-
 butyldiphenylsilyl methyl maleate, t-butyldiphenylsilyl n-
 butyl fumarate, t-butyldiphenylsilyl n-butyl maleate,
 triisopropylsilyl amyl fumarate, triisopropylsilyl amyl
 15 maleate, triisopropylsilyl methyl fumarate,
 triisopropylsilyl methyl maleate, tri-n-butylsilyl n-butyl
 fumarate, tri-n-butylsilyl n-butyl maleate, and the like
 and polymers or copolymers thereof, wherein methacrylate
 or acrylate is herein collectively referred to as a
 20 "(meth)acrylate".

In a preferred embodiment, said organosilylated
 carboxylate of formula (II) is selected from the group
 comprising trimethylsilyl (meth)acrylate, tri t-butylsilyl
 (meth)acrylate, tribenzylsilyl (meth)acrylate,
 25 triethylsilyl (meth)acrylate, tri-isopropylsilyl
 (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-n-
 amylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate,
 tri-n-dodecylsilyl (meth)acrylate, tri-n-hexylsilyl
 (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-
 30 propylsilyl (meth)acrylate and triphenylsilyl
 (meth)acrylate and copolymers or polymers thereof. More
 preferably said organosilylated carboxylate of formula

(II) is trimethylsilyl methacrylate or a copolymer or a polymer thereof.

This process can be suitably applied to unsaturated organosilylated carboxylate copolymers or polymers. The reaction is performed in such a way that the trialkylsilyl carboxylate functions present in the copolymer or polymer are selectively converted into polyorganosilyl function. Suitable unsaturated organosilylated carboxylate copolymers or polymers can be obtained using processes known in the art by polymerisation of unsaturated organosilylated carboxylate monomers of formula (II), and/or by polymerisation with various other monomers such as vinyl monomers including acrylic esters, methacrylic esters, styrene, vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate), vinyltoluene, alpha-methylstyrene, crotonic esters, and itaconic esters. The polymers or copolymers of the unsaturated organosilylated carboxylate of formula (II) can be prepared by addition polymerisation of the appropriate monomers in the appropriate proportions at polymerisation conditions using a free radical catalyst such as e.g. benzoyl peroxide, tert-butyl peroxy 2-ethyl hexanoate (TBPEH), t-butyl peroxybenzoate (TBP), or azobisisobutyronitrile. The reaction is carried out in an organic solvent such as e.g. xylene, toluene, amides such as N-methylpyrrolidone and N,N-dimethylformamide, ethers such as dioxane, THF and diethyl ether, butyl acetate, n-butanol, 2-ethoxyethanol, cyclohexanone, methyl-isoamyl ketone, 2-methoxyethanol, 2-butoxyethanol, 2-ethoxyethyl acetate, and mixtures thereof. Polymerisation is preferably carried out at a temperature in the range of 70-140°C although higher temperatures may be used providing that the solvent and the catalyst are adapted

thereto. Within this range the use of higher temperatures produces polymers of lower molecular weight. Polymerisation maybe carried out by heating all the polymer ingredients in the solvent or preferably by
5 gradually adding the monomers and catalyst to the heated solvent. The latter procedure produces polymers of lower molecular weight.

Examples of suitable catalyst for the reaction include but are not limited to acidic catalyst. Examples of acid
10 catalysts include proton acid catalysts and Lewis acid catalysts. In a preferred embodiment, the proton acid catalysts suitable for use in the present process include but are not limited to hydrochloric acid, nitric acid, acetic acid, sulfuric acid, trifluoromethanesulfonic acid,
15 trifluoroacetic acid. In a preferred embodiment, trifluoromethanesulfonic acid is used. Said acid catalyst may be a heterogeneous acids such as the strongly acidic ion exchange resins, all of which are of the sulfonic type. Examples of commercially available strongly acidic
20 ion exchange resins of the sulfonic type are those known by the trade names AMBERLYST A15, AMBERLYST 38 W, AMBERLYST 36, AMBERJET 1500H, AMBERJET 1200H, (AMBERJET is a trademark of Rohm and Haas Company) DOWEX MSC-1, DOWEX 50W (DOWEX is a trademark of Dow Chemical Company),
25 DELOXAN ASP I/9 (DELOXAN is a trademark of Degussa), DIAION SK1B (DIAION is a trademark of Mitsubishi), LEWATIT VP OC 1812, LEWATIT S 100 MB, LEWATIT S 100 G1 (LEWATIT is a trademark of Bayer), NAFION SAC13, NAFION NR50 (NAFION is a trademark of DuPont) and CT275 (a macroporous resin
30 with a medium pore diameter in the range of from 600 to 750, available from Purlite). In another embodiment, suitable Lewis acid catalysts include but are not limited to ZnCl_2 , BeCl_2 , TiCl_4 , SnCl_4 , FeCl_3 , FeCl_2 , SbCl_5 , AlCl_3

and other metal halides. Co-catalysts such as acetic acid may also be used in the process according to the invention.

Because they permit the suppression of equilibration
5 reactions due to siloxane bond rearrangement, selectively bringing about the ring-opening reaction of the cyclosiloxane, and can suppress undesirable side reactions, metal halides exhibiting Lewis acid properties are particularly useful. In a preferred embodiment, the
10 catalyst used during the reaction is ZnCl_2 . When a heterogeneous acid is used in the process according to the invention, this has the advantage of easier separation from the reaction product. In a preferred embodiment, AMBERLYST A15 is used. When the reaction is performed with
15 copolymers of unsaturated organosilylated carboxylate, the use of heterogeneous catalysts is preferred because it offers the advantage of being easily removed from the resin at the end of the process.

The telomerisation reaction between the cyclosiloxane and
20 the unsaturated organosilylated carboxylate can be preformed at a temperature selected in the range of 20 to 150 °C, preferably 50 to 120 °C, more preferably 90 to 110 °C. In another preferred embodiment said reaction is performed at room temperature.

25 The reaction may be conducted with or without added polymerisation inhibitor. The polymerisation inhibitors which can be used in the process of the invention are preferably phenolic stabilizers such as cresol or hydroquinone derivatives, e.g. bis(tert-butyl)cresol, 2,5-
30 di-tert-butylhydroquinone, 4-methoxy-phenol, 2,6-di-tert-butyl-4-methylphenol or the monomethyl ether of hydroquinone or phenothiazine, in a concentration ranging from 0.001% to 2% by weight, preferably from 0.002% to

0.7% by weight, based on the total weight of cyclosiloxane and unsaturated organosilylated carboxylate (II).

The ring-opening reaction may be terminated by neutralizing the acidic catalyst with a suitable base
5 which may be selected from the group comprising triethylamine, diethylamine, tributylamine, hexamethyldisilazane N-methylmorpholine, diisopropylethylamine, dicyclohexylamine, N-methylpiperidine, pyridine, 4-pyrrolidinopyridine, picoline, 4-(N,N-dimethylamino)pyridine, 2,6-di(t-butyl)-
10 4-methylpyridine, quinoline, N,N-dimethylaniline, N,N-diethylaniline and the like. In a preferred embodiment said base is triethylamine. The salts produced during this neutralization reaction can be removed by filtration or
15 decantation.

The polyorganosilylated carboxylate compound of formula (I) can be isolated by distillation under reduced pressure. The reaction progress may be monitored by any suitable analytical method. The polymer of
20 polyorganosilylated carboxylate compound of formula (I) can be isolated by filtrating the catalyst at the end of the reaction.

The present invention further relates to polyorganosilylated carboxylate monomers of formula (I) or
25 polymers thereof, which may be obtainable by the process according to the invention. In another embodiment the present invention relates to polyorganosilylated carboxylate monomers or polymers obtained by the process according to the invention. In a preferred embodiment, R¹,
30 R², R³, R⁴, R⁵, R⁶ and R⁹ in compound of formula (I) are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl. More preferably R¹, R², R³, R⁴, R⁵, R⁶ and

R⁹ are methyl. In another preferred embodiment, n is selected such as to represents a number of dihydrocarbylsiloxane units from 3 to 12, preferably from 3 to 8, more preferably from 3 to 6. In a more preferred
 5 embodiment, n is 3.

Examples of the polyorganosilylated carboxylate monomers obtained by the process of the invention include but are not limited to

	nonamethyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nonaethyl-1-(meth)acryloyloxy-
10	tetrasiloxane,
	nona-t-butyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nonabenzyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nona-isopropyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nona-n-propyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nona-isobutyl-1-(meth)acryloyloxy-
15	tetrasiloxane,
	nona-amyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nona-n-butyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nona-dodecyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nona-hexyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	nona-phenyl-1-(meth)acryloyloxy-
20	tetrasiloxane,
	nona-octyl-1-(meth)acryloyloxy-
	tetrasiloxane,
	undecamethyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undecaethyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-t-butyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undecabenzyl-1-(meth)acryloyloxy-
25	pentasiloxane,
	undeca-isopropyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-n-propyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-isobutyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-amyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-n-butyl-1-(meth)acryloyloxy-
30	pentasiloxane,
	undeca-dodecyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-hexyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-phenyl-1-(meth)acryloyloxy-
	pentasiloxane,
	undeca-octyl-1-(meth)acryloyloxy-

	pentasiloxane	tridecamethyl-1-(meth)acryloyloxy-
	hexasiloxane,	tridecaethyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-t-butyl-1-(meth)acryloyloxy-
	hexasiloxane,	tridecabenzyl-1-(meth)acryloyloxy-
5	hexasiloxane,	trideca-isopropyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-n-propyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-isobutyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-amyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-n-butyl-1-(meth)acryloyloxy-
10	hexasiloxane,	trideca-dodecyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-hexyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-phenyl-1-(meth)acryloyloxy-
	hexasiloxane,	trideca-octyl-1-(meth)acryloyloxy-

hexasiloxane and polymers thereof.

15 The advantage of this invention is that the process uses reactants, which can be easily handled. Another advantage lies in the simplicity and safety of the procedure (no trapping of corrosive gaseous matter). Furthermore, another advantage is that the reaction is a one step

20 procedure. Also no degradation of the material occurs. Due to its shortness, its easy work-up procedure and its high yield the process of the present invention can be considered as a substantial improvement over the existing methods described above.

25 Still another advantage of the invention is that the polyorganosilylated carboxylate monomers or polymers obtained by the process according to the invention have the exactly desired number of dihydrocarbylsilyloxy units. The polyorganosilylated carboxylate monomers obtained by

30 the process of the invention can be polymerised with various other monomers such as vinyl monomers including acrylic esters, methacrylic esters, styrene, vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl butyrate,

vinyl benzoate), vinyltoluene, alpha-methylstyrene, crotonic esters, and itaconic esters.

The polymers and copolymers of said monomers are useful in coating or paint composition. More preferably they are
5 used as comonomer unit in the binder of antifouling coating compositions. When used in an antifouling coating composition, they give a film which undergoes neither cracking nor peeling and shows moderate hydrolysability to dissolve into seawater constantly at an adequate rate and
10 which therefore exhibits excellent antifouling property for long term.

The antifouling coating compositions prepared using the monomers obtained by the process of the invention are tin-free coatings and provide an alternative to the present
15 self-polishing coating technology based on hydrolysable tributyltin polymers (the use of which is due to be banned in antifouling paints by 2003). The polyorganosilylated carboxylate monomers provided by the process of the invention compared to organotin compounds are less toxic,
20 less polar, more hydrophobic and more stable.

The invention will be more readily understood by reference to the following examples, which are included merely for purposes of illustration of certain aspects and embodiments of the present invention and are not intended
25 to limit the invention.

Examples

In the following examples, NMR data have been determined in CDCl₃ and are expressed as delta versus TMS. Unless otherwise stated, all the reactants were purchased from Aldrich and were used without purification.

Example 1:

50 g of hexamethylcyclotrisiloxane, 35.6 g of trimethylsilyl methacrylate, 2.5 g of zinc chloride and 0.4 g of 4-methoxy phenol were dissolved in 50 ml of toluene. After 11 h at 100°C, the mixture was allowed to cool until room temperature, 40 ml of triethylamine were then added and the salts were filtered. After evaporation of the solvent, distillation under reduced pressure (0.3 mbar, 80°C) furnished pure nonamethyl-1-methacryloyloxy-tetrasiloxane.

¹³C NMR: 167.0, 137.7, 126.4, 18.5, 2.0, 1.3, 1.1, 0.0;
²⁹Si NMR: 7.3, -8.6, -20.1, -21.0;
IR (film): 2963, 1707, 1638, 1335, 1310, 1261, 1179, 1082, 1044, 842, 804 cm⁻¹.

Example 2:

5 g of hexamethylcyclotrisiloxane, 3.5 g of trimethylsilyl methacrylate, 0.016 g of trifluoromethane sulfonic acid were stirred for 24h at room temperature. 0.5 ml of triethylamine was then added, and the salts were filtered to furnish nonamethyl-1-methacryloyloxy-tetrasiloxane.

Example 3

5 g of hexamethylcyclotrisiloxane, 3.5 g of trimethylsilyl methacrylate and 0.3 g of Amberlyst A15 resin catalyst were stirred in 2.5 ml of toluene. After 7h at room temperature the catalyst was filtered and the solvent evaporated under reduced pressure to furnish nonamethyl-1-methacryloyloxy-tetrasiloxane.

The use of AMBERLYST A15 resin catalyst, which is an insoluble acidic resin, provides the advantages of

allowing a clean transformation at room temperature.
Furthermore it is easily removed by filtration.

Example 4

5 g of hexamethylcyclotrisiloxane, 4.4 g of triethylsilyl methacrylate and 0.3 g of Amberlyst A15 resin were stirred in 2.5 ml of toluene. After 7 h at room temperature, the catalyst was filtered and the solvent evaporated under reduced pressure to furnish 1,1,1-triethyl-2,2,3,3,4,4-hexamethyl-1-methacryloyloxy-tetrasiloxane.

The compound was characterised by GC-MS. Column: HP5 (30 m/i.d.:0.32 mm i.d./thickness:0.25 microns), initial temperature: 70°C, final temperature: 300°C, rate: 10°C/min, retention time: 11.2 min. EIMS: M⁺: 422 (<1%), 407 (100%), 393 (85%), 309 (5%), 253 (10%), 217 (10%); IR (film): 2961, 2881, 1704, 1637, 1336, 1261, 1178, 1088, 1023, 808 cm⁻¹.

Example 5

100 g of xylene was added to a 2l 4-necks flask and kept under nitrogen. The four necks of the flask were equipped with stirrings means, a reflux condenser, a thermometer for temperature control of the reaction, and means for addition of the monomers.

A premix was prepared in a separate vessel, containing:

- 148.5 g of methyl methacrylate
- 346.5 g of butyl acrylate
- 49.5 g of trimethylsilyl methacrylate
- 25 -9.9 g (=2% on total monomer weight) t-Butyl peroxy-2-ethyl hexanoate (=TBPEH sold under the name Trigonox 21S by Akzo-Nobel)

The premix was added drop by drop to the reaction vessel (total time = 3 hours) whilst maintaining the temperature at 90°C. Thirty minutes after the end of the addition of the premix, five post-additions of 0.1% TBPEH were made at intervals of 45 minutes. 15 minutes after the last post addition, the temperature was increased up to 120°C during one hour. After cooling the binder solution was thinned with 98 g of xylene to a viscosity of 14 dPa.s.

66.5 g of hexamethylcyclotrisiloxane and 1 g of Amberlyst A15 resin were added to the binder. After 5 h at room temperature, the catalyst was filtered and the binder was diluted with xylene to a viscosity of 14 dPa.s.

- 5 The NMR spectra of the obtained polymer was found to be identical to the NMR spectra of the polymer obtained by polymerising nonamethyl-1-methacryloyloxy-tetrasiloxane.

It was surprisingly found that the telomerisation of hexamethylcyclotrisiloxane could be performed with silyl
10 methacrylates or polymers or copolymers thereof, which were known to be less reactive, and prone to polymerisation. A clean conversion was observed (GC) and no oligomerisation of the formed polysilyl methacrylate was observed. The product was easily purified by
15 distillation. When the polymer was synthesised, it was isolated by simply eliminating the catalyst.

The process according to the invention has the advantage of being a one step process. Moreover during said process there is no release of corrosive matter. The purification
20 of the product produced is straightforward and there is a good control of the MW of the polydimethyl siloxane produced. Furthermore the polydialkylsiloxane units do not undergo fragmentation or oligomerisation during the reaction.

- 25 While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.